



PATENT
2001-1120-1

IN THE U.S. PATENT AND TRADEMARK OFFICE

In re application of

Cees Jan Nico BUISMAN et al. Conf. 4457

Application No. 10/720,102 Group 1754
(continuation of 09/831,950)

Examiner T. Vanoy

Filed November 25, 2003

PROCESS FOR THE PRODUCTION OF
HYDROGEN SULPHIDE FROM ELEMENTAL
SULHUR AND USE THEREOF IN HEAVY
METAL RECOVERY

SUBMISSION OF DECLARATION UNDER 37 CFR §1.132

Assistant Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

March 17, 2004

Sir:

Prior to the first Official Action on the merits, applicants wish to make of record the accompanying Declaration Under 37 CFR §1.132 from Mr. Jacob Leendert HUISMAN, an expert in the field of biological wastewater treatment plants.

In his declaration, Mr. HUISMAN declares that the hydraulic retention time as used in the instant continuation application is essentially the mean residence time of the liquid reactor medium containing the sulfur-reducing bacteria in the bioreactor. Mr. HUISMAN further declares that the instant application prescribes a hydraulic retention or residence time of at least one day, and preferably at least 5 days, as is claimed

in independent claim 1. Mr. HUISMAN notes from the present specification and examples, that applicants do not use any means for retaining the bacteria in the bioreactor whose contents are mixed. Mr. HUISMAN concludes that the residence time of the bacteria is approximately equal to the hydraulic retention time.

Mr. HUISMAN goes on to explain that a hydraulic retention time is quite different from a reaction rate, which is commonly defined as the amount of mass of reaction partners that is converted per time unit. The addition of reaction partners does not influence the hydraulic retention time, because the elemental sulfur is effectively added as a solid and the electron donor is added as a gas or a concentrated organic substance.

Mr. HUISMAN concludes that the hydraulic retention time defines the residence time of the liquid and biomass in the reactor, whereas the reaction time is related to the presence of the reaction partners. Where at least one reaction partner is added independently from the liquid flow, the two are also factually unrelated.

The declarant goes on to infer from the relevant prior art, including International Publication WO 92/17410, that conventional biological processes for reducing sulfur compounds always use relatively short hydraulic retention times, commonly on the order of a few hours, and that separators, filters, solid carriers and similar devices are used for maintaining the

bacteria in the bioreactor. The hydraulic residence time of the process described in International Publication WO 92/17410 is as short as possible, in order to treat as much wastewater as possible with a given reactor volume. This is to be contrasted with the herein-claimed invention, which has a hydraulic residence time as long as possible, in order to minimize the bleed as much as possible. This is because the reagents are added as solids and pure liquids, whereas the product is removed in a gas phase.

In light of the above, it is Mr. HUISMAN's conclusion that the herein-claimed invention is substantially different from the prior art processes, since the international publication fails to disclose or suggest a hydraulic retention time in the bioreactor of at least 5 days. This hydraulic retention time is orders of magnitude greater than the 4 hours disclosed in the international publication, and consequently would not have been obvious to the skilled artisan.

In light of the accompanying 37 CFR §1.132 declaration, it is believed that original claims 1-14 patentably distinguish from the international publication applied in parent application Serial No. 09/831,950.

A prompt and favorable first action on the merits is accordingly earnestly solicited.

Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Applicant: Buisman et al.

Serial No.: 10/720,102
(continuation of 09/831,950)

Filed: November 25, 2003

Title: Process for the Production of Hydrogen Sulphide from Elemental Sulphur and Use thereof in Heavy Metal Recovery

Group: 1754

Examiner: T. Vanoy

February 5, 2004

DECLARATION UNDER 37 CFR SECTION 132

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

Sir:

I, Jacob Leendert Huisman, residing at Pijlkruidhof 29, 8446 BV Heerenveen, The Netherlands, do hereby declare that:

1. I am a citizen of the Netherlands,
2. My educational and technical background in the field of Chemical and Bioprocess Technology is as follows:
 - a) I am a M.Sc. graduate from the Department of Chemical Engineering, Delft

University of Technology, The Netherlands, specialisation bioprocess technology in 1993 (with distinction) and a Ph.D. graduate from the Swiss Federal Institute of Technology, Zürich, Switzerland (ETHZ) in 2001 (designated Best Thesis of the Year in Aquatic Sciences);

b) From 2001 till 2002, I was employed at the University of Tokyo as a postdoctoral researcher, modelling biological wastewater treatment plants

c) I have been employed by Paques BV since 2002, presently as a Technology Manager Sulfate Technology dealing with research and the process design of full scale installations for biological sulfate and metal removal.

3. I have read Buisman et al. US application 09/831,950 filed May 6, 2001;
4. I declare the following with regard to the question of hydraulic retention times (similarly known as mean hydraulic residence time) as used in the Buisman et al. application:

In the art of Process Engineering of chemical reactors and bioreactors, the mean hydraulic residence time is defined as the volume of the reactor tank divided by the liquid flow through the tank¹:

$$t_r = V/Q$$

where t_r = Hydraulic residence time, mean [d]

V = Volume of the contents of the tank [m³]

Q = volumetric throughput [m³/d].

I understand the hydraulic retention time as used in the present Buisman et al. application as the mean residence time of the liquid reactor medium containing the sulfur-reducing bacteria in the bioreactor. I note that Buisman et al. prescribe a hydraulic residence time of at least one day and preferably between 5 days and 1 month.

I note furthermore from the specification and the examples that Buisman et al. do not use a means retaining the bacteria in the reactor. In addition, the reactor contents is mixed. I conclude therefore that the residence time of the bacteria is approximately equal to the hydraulic retention time.

¹ J.M. Coulson and J.F. Richardson, Chemical Engineering, vol. 1: Fluid flow, Heat transfer and mass transfer, 4th ed., Pergamon Press, Oxford, UK, p.260.

I also note that the starting materials for the bacterial conversion, the elemental sulfur on the one hand and the electron donor (gaseous hydrogen, gaseous carbon monoxide or a pure solution of an organic electron donor) on the other hand, are added to the reactor, independently from the liquid flow. The solid sulfur is dispersed in the reactor liquid and added as a slurry to the bioreactor. In other words, the addition of solid sulfur (second reaction partner) has no influence on the hydraulic retention time.

Furthermore, the product of the bacterial conversion is hydrogen sulphide, which is withdrawn from the reactor with the help of a stripping gas, independently from the liquid flow.

As a result, the bacterial conversion rate is not dependent on the liquid flow, i.e. the hydraulic retention time. The function of the liquid flow is basically to remove waste products (inerts) from the bioreactor and to control pH and conductivity, *not* to transport the product of the process, i.e. the hydrogen sulfide, to another process unit.

A hydraulic retention time is different from a reaction rate. A reaction rate is commonly defined as the amount of mass of reaction partners that is converted per time unit. This is expressed in the form of the rate law, mathematically written as²:

$$r_{H2S} = k * f(C_{e\text{-donor}}, C_{\text{Sulfur}})$$

where

r_{H2S} = Production rate of hydrogen sulfide [kg/m³/d]

k = Reaction rate constant [1/d]

$C_{e\text{-donor}}$ = Concentration of electron donor (first reaction partner) [kg/m³]

C_{Sulfur} = Concentration of sulfur (second reaction partner) [kg/m³]

This addition of the reaction partners does not influence the hydraulic retention time because the elemental sulfur is effectively added as a solid and the e-donor is added as a gas or a concentrated organic substance.

Thus, the hydraulic retention time defines the residence time of the liquid and biomass in the reactor, whereas the reaction time is related to the presence of the reaction partners. Where at least one reaction partner is added independently from

² H.Scott Fogler, Elements of Chemical Reaction Engineering, Prentice-Hall Inc., Engelwood Cliffs, New Jersey, 2001, p.60.

the liquid flow, the two are also factually unrelated.

I infer from the relevant prior art, including WO 92/17410, that conventional bacterial process for reducing sulfur compounds always use short hydraulic retention times, commonly in the order of a few hours, and that separators, filters, solid carriers and similar devices are used for maintaining the bacteria in the reactor. The hydraulic residence time of the process in WO 92/17410 is as short as possible in order to treat as much wastewater as possible with a given reactor volume.

The process as claimed in the present Buisman et al. application has a hydraulic residence time that is as long as possible in order to minimize the bleed as much as possible. This is possible because the reagents are added as solids and pure liquids, whereas the product is removed through the gas phase.

Therefore the process as claimed in the present Buisman et al. application is essentially different from the prior art processes.

5. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: Heerenveen February 5, 2004
(place) (date)

Signature: 

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Indeed, the devices described all exist in a variety of configurations. In addition, there are many items of equipment based on altogether different principles; typical examples include jet mixers, in-line dynamic mixers, mills, valve homogenisers, ultrasonic homogenisers, etc. These, as well as many other types, have been discussed by HARNBY *et al.*⁽²⁾, OLDSHUE⁽¹¹⁾, and NAGATA⁽¹⁹⁾.

Frequently, it is convenient to mix the contents of a tank without the necessity for introducing an agitator and this may present difficulties in the construction of the vessel. It may then be possible to use an external circulating pump (usually centrifugal). If it is desirable not to make special connections to the vessel, it may be possible to connect the suction side of the pump to the bottom outlet of the tank by means of a T-piece and to discharge the liquid into the tank through its open top or through an existing entry point. In such a system, dispersion is effected in the high-shear region in the pump, and the liquid in the tank is maintained in a state of continuous circulation.

Such an arrangement may well be suitable when it is necessary to prevent fine particles from settling out at the bottom of the tank.

7.8. MIXING IN CONTINUOUS SYSTEMS

The mixing problems considered so far have related to batch systems in which two materials are mixed together and uniformity is maintained by continued operation of the agitator.

Frequently, stirred tanks are used with a continuous flow of material in on one side of the tank and with a continuous outflow from the other. A particular application is the use of the tank as a continuous-stirred-tank-reactor (CSTR). Inevitably, there will be a very wide range of residence times for elements of fluid in the tank. Even if the mixing is so rapid that the contents of the tank are always uniform in composition, some elements of fluid will almost immediately flow to the outlet point and others will continue circulating in the tank for a very long period before leaving. The *mean residence time* fluid in the tank is given by:

$$t_r = \frac{V}{Q} \quad (7.23)$$

where V is the volume of the contents of the tank (assumed constant), and Q is the volumetric throughput.

In a completely mixed system, the composition of the outlet stream will be equal to the composition in the tank.

The variation of time for which fluid elements remain with the tank is expressed as a *residence time distribution* and this can be calculated from a simple material balance if mixing is complete. For incomplete mixing, the calculation presents difficulties.

The problem is of great significance in the design of reactors because a varying residence time will, in general, lead to different degrees of chemical conversion of various fluid elements, and this is discussed in some detail in Volume 3, Chapter 1.

7.9. FURTHER READING

HARNBY, N., EDWARDS, M. F., and NIENOW, A. W. (eds.): *Mixing in the Process Industries* 2nd edn. (Butterworth Heinemann, London, 1992).
HOLLAND, F. A. and CHAPMAN, F. S.: *Liquid Mixing and Processing in Stirred Tanks* (Reinhold, New York, 1966).

Rate Laws and Stoichiometry 3

Facts are stupid until brought into connection with some general law.

Louis Agassiz (1807-1873)

We have shown that in order to calculate the time necessary to achieve a given conversion X in a batch system, or to calculate the reactor volume needed to achieve a conversion X in a flow system, we need to know the reaction rate as a function of conversion. In this chapter we show how this functional dependence is obtained. First there is a brief discussion of chemical kinetics, emphasizing definitions, which illustrates how the reaction rate depends on the concentrations of the reacting species. This is followed by instructions on how to convert the reaction rate law from the concentration dependence to a dependence on conversion. Once this is achieved, we can design a number of isothermal reaction systems.

3.1 Basic Definitions

A *homogeneous reaction* is one that involves only one phase. A *heterogeneous reaction* involves more than one phase, and reaction usually occurs at or very near the interface between the phases. An *irreversible reaction* is one that proceeds in only one direction and continues in that direction until the reactants are exhausted. A *reversible reaction*, on the other hand, can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations. An irreversible reaction behaves as if no equilibrium

Types of reactions

condition exists. Strictly speaking, no chemical reaction is completely irreversible, but in very many reactions the equilibrium point lies so far to the right that they are treated as irreversible reactions.

3.1.1 The reaction rate constant

In the chemical reactions that are considered in the following paragraphs, we take as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A, $-r_A$, depends on temperature and composition. For many reactions it can be written as the product of a *reaction rate constant* k and a function of the concentrations of the various species involved in the reaction, i.e.,

The rate law gives the relationship between reaction rate and concentration

$$-r_A = [k(T)][f_n(C_A, C_B, \dots)] \quad (3-1)$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the **kinetic expression** or **rate law**.

The reaction rate constant k is not truly a constant, but is merely independent of the concentrations of the species involved in the reaction. The quantity k is also referred to as the **specific reaction rate (constant)**. It is almost always strongly dependent on temperature. In gas-phase reactions, it depends on the catalyst and may be a function of total pressure. In liquid systems it can also be a function of total pressure, and in addition can depend on other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much less effect on the specific reaction rate than does temperature, so for the purposes of the material presented here it will be assumed that k depends only on temperature. This assumption is valid in most laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that the temperature dependence of the specific reaction rate, k , could be correlated by an equation of the type

Arrhenius equation

$$k(T) = Ae^{-E/RT} \quad (3-2)$$

where $A \equiv$ preexponential factor or frequency factor

$E \equiv$ activation energy, J/mol or cal/mol

$R \equiv$ gas constant = 8.314 J/mol·K = 1.987 cal/mol·K

$T \equiv$ absolute temperature, K

Equation (3-2), known as the *Arrhenius equation*, has been verified empirically to

give the temperature behavior of most reaction rate constants within experimental accuracy over fairly large temperature ranges.

The activation energy E has been equated with a minimum energy which must be possessed by reacting molecules before the reaction will occur. From the kinetic theory of gases, the factor $e^{-E/RT}$ gives the fraction of the collisions between molecules that together have this minimum energy E . Although this might be an acceptable elementary explanation, recent work indicates that E is nothing more than an empirical parameter correlating the specific reaction rate with temperature.[†] Nevertheless, postulation of the Arrhenius equation remains as the greatest single step in chemical kinetics, and retains its usefulness today, almost a century later.

The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of equation (3-2),

Calculation of the activation energy

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad (3-3)$$

it can be seen that a plot of $\ln k$ versus $1/T$ should be a straight line whose slope is proportional to the activation energy.

Example 3-1 Determination of the Activation Energy

Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen, i.e.,



using the following information for this first-order reaction:

k (s ⁻¹)	0.00043	0.00103	0.0180	0.00355	0.00717
T (K)	313.0	319.0	323.0	328.0	333.0

Solution

By converting equation (3-3) to log base 10, i.e.,

$$\log k = \log A - \frac{E}{2.303R} \left(\frac{1}{T} \right) \quad (E3-1.1)$$

we can use semilog paper to determine E quite readily by first forming the

[†]M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, 43, 3259 (1965); D. G. Truhlar, *J. Chem. Educ.*, 55(5), 310 (1978).